



Battery composition

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List of abbreviations

BMS	Battery Management System
LFP	Lithium Iron Phosphate
LIB	Lithium-ion battery
LCO	Lithium Cobalt Oxide
LMO	Lithium Manganese Oxide
NCA	Nickel Cobalt Aluminate
NMC	Nickel Manganese Cobalt Oxide
LTO	Lithium Titanium Oxide
NTO	Niobium Titanium Oxide



Summary

Battery technology developments have progressed quickly and batteries have been employed for many types of applications: from small portable devices, such as mobiles and laptops containing batteries of maximum 300 grams, to electric vehicles and heavy duty applications holding batteries of several hundreds of kilograms. The demand for batteries as a result of the energy transition requires large amounts of materials; however, the European Union does not hold sufficient mines to meet this demand. Therefore, many initiatives for recycling of batteries have been announced to recover such critical materials from the European urban mine. The European Battery Regulation already set minimum recovery levels of certain elements contained in batteries, such as cobalt (85%), lead (6%), lithium (6%) and nickel (6%) from manufacturing and consumer waste to be reused in new batteries. The Netherlands and Dutch companies have addressed the urgency as well: the requirement of a battery value chain to secure battery materials and components needed for the energy transition in the Netherlands. In this regard, it is expected for the Dutch economy to be completely circular by 2050 and to reduce by half the consumption of primary raw materials on 2030. These goals are aligned to the 2030 Sustainable Development Goals and the Paris Agreement.

One of the first steps to achieve a solid battery value chain is to do a technology assessment of both the battery technologies as well as the recycling technologies. This report gives an overview of the battery technologies with a specific focus on cathode active materials, now and in the future, and explores the impact of different battery chemistries on the recycling of the materials.

In the past decades, a wide variety of cathode active materials has been developed, mostly focused on the use of lithium, cobalt, nickel and manganese. Changes of the cathode active material composition have been driven by four important factors in general: the concentration of cobalt has been lowered as a result of high cost for cobalt as well as poor labor conditions in the cobalt mines. Then, to improve the performance of batteries, the concentration of nickel has been increased. Finally, the use of lithium iron phosphate as a cathode active material has significantly lowered the price of batteries, making them interesting for e.g. heavy duty applications.

Batteries are complex products containing a wide variety of materials. However, depending on the complexity of the construction of the battery, a number of components, casing and electronics can be manually dismantled for high-quality recycling. Other components, such as the cell casing, current collectors and active materials cannot be dismantled, but are comminuted and in this way mixed together. Most recycling technologies employ a pre-treatment step, including several separation steps, starting with cell discharging, autoclaving/shredding and further separation steps, preceding a hydrometallurgical processing route, which yields an intermediate product, black mass. Black mass mostly contains the active materials from the cathode and anode, comprising approximately 25 % of the total battery weight, but also small particles from current collectors and separators, for example. The latter represent circa 40 % of the total battery weight, but are mostly separated from the black mass fraction in the pre-treatment process.

Future battery technologies will complicate the design of a one-process-fits-all design: new battery technologies use additional elements, titanium in the case of LTO and NTO anodes and silicon for Si-C anodes, or contain more complicated structures, as in the case of quasi solid state batteries. However, on the short term, these battery technologies are not expected to be recycled as they are not yet produced on an industrial scale. By the time such batteries are produced at such scale and reach end-of-life, sorting preceding comminution becomes important. Therefore, the first significant end-of-life streams will mainly contain batteries with NMC, NCA and LFP chemistry.

The composition of the intermediate product of battery recycling technologies, black mass, is as mentioned strongly dependent on the chemistry of batteries comminuted in the pre-treatment process. A mix of battery chemistries fed to the pre-treatment process yields a wide variety of elements in the

black mass, possibly complicating the recycling process and must force recyclers to implement a thorough sorting step in the process. In addition, the pre-treatment separation steps are also crucial for the efficiency of the recovery of cathode specific materials.



1. Introduction

In the 1980's with a rapidly growing demand for batteries to be used in portable electronics like the walk man, ever larger transistor radios and cellular phones, see Figure 1, the holy grail of portable power was a lightweight, preferably rechargeable, battery. The first rechargeable batteries were mostly based on lead-acid and nickel-cadmium chemistry. Nickel metal hydride batteries meant a serious step forward in terms of specific energy and power, but this was insufficient for more demanding applications such as laptops. (Liang et al., 2019) Sony was the first company to introduce lithium-ion batteries in a commercial application in 1991. With no other rechargeable battery technology available to surpass its specific energy and power, it has become the dominant technology for portable applications. First in small appliances such as mobile phones and cameras, currently being employed in electric vehicles, trucks and energy storage systems to enable the energy transition.



Figure 1: Timeline of the development of the application of lithium-ion batteries in a variety of portable devices. Copied from reference (Liang et al., 2019).

In the ongoing transition to more sustainable ways of energy distribution, batteries have become a major instrument for enabling future technology. For most mobility overland, road traffic as well as rail, electrification with or without batteries has appeared to be a very attractive way forward. In the Netherlands, battery electric vehicles sales have increased 123% on 2023 with respect to last year, with 320,987 units registered in the first quarter of this year, representing a 43.2% rise. (ACEA, 2023) In general, one could conclude that the majority of overland transport will become electric in the next couple of decades. A very large portion of the electric vehicles (e.g., cars, heavy duty vehicles such as trucks) will be powered by batteries, and presently lithium-ion batteries (LIBs) are the dominant technology, as they have the best fitting set of characteristics for this application. Moreover, shipping and energy storage are two other relevant applications of batteries. In the case of energy storage, once electric vehicles batteries reach their life span and can no longer be used to power vehicles, they can be reused as stationary energy battery storage systems, as a means to store energy for less energy and power density demanding applications.

It is for this reason that the major LIB manufacturers foresee a considerable growth of their markets in this decade, which is also supported by many announcements of new production facilities in Europe, see Figure 2.

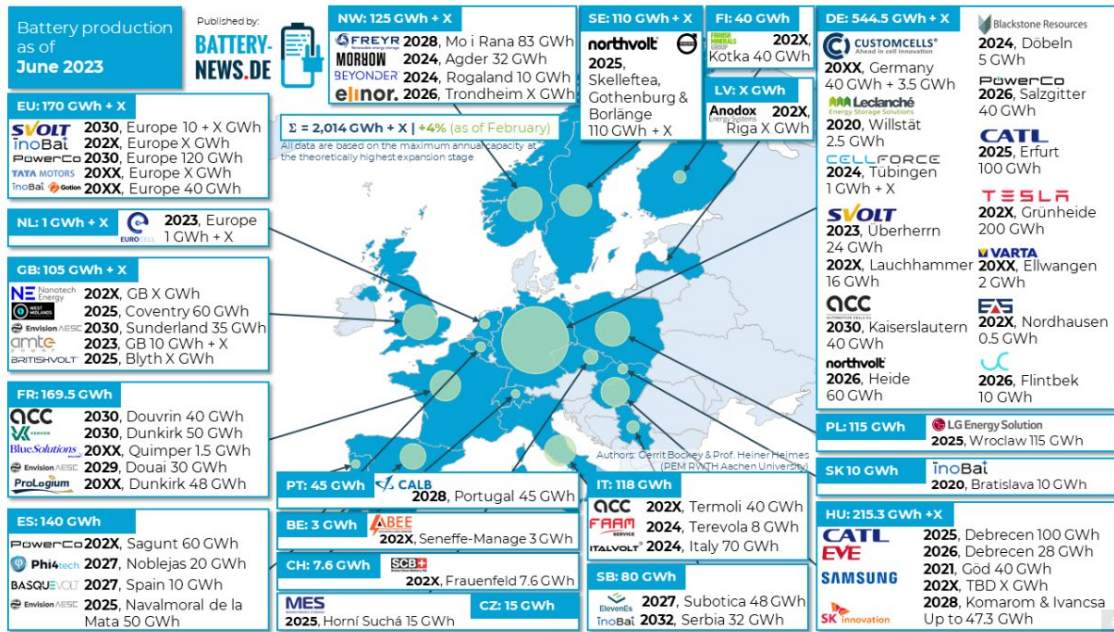


Figure 2: An overview of all battery cell production facilities announced up to June 2023.(Battery-News.de, 2023)

The sharp growth in volumes of Li-ion batteries manufactured will lead to a rapid increase in demand for feedstock materials. The present instability in world markets due to the Corona pandemic as well as the war that started in Ukraine, gave an additional urgency for re-thinking of supply-security. Since most countries do not have geological mines, extraction of materials from waste streams must contribute to a certain level of independency. The Dutch government as well as Dutch companies have expressed similar concerns and are aware that although the Netherlands do not have geological mines, the urban mine is present in the form of lithium-ion batteries in electric vehicles. Battery recycling however, is not yet part of the Dutch battery value chain. Therefore, in order to establish solid battery recycling activities from the beginning, one must examine the current battery market and the current battery recycling technologies. These activities are the first two tasks of Work Package 6: the first task focuses on the analysis of the battery technologies which are currently in production as well as future battery technologies. The second task examines the state of the art battery recycling technologies, with a specific focus on NMC and LFP batteries. As most technologies for recycling NMC batteries also contain a process step recovering aluminum, NCA batteries are also taken into account when investigating the recycling of NMC batteries. Therefore, there will be no specific focus on recycling technologies for NCA batteries. Finally, the work package will also deliver an analysis of the most optimum combination of recycling technologies based on the best available technologies.

This report will give an overview of the developments in lithium-ion battery technology. Chapter 2 outlines the composition of the components in lithium-ion batteries currently being put on market. Not only the main interesting materials, the cathode active materials will be described, also materials such as the current collectors and electrolyte will be discussed as such materials strongly influence the recycling of the cathode active materials. Chapter 3 examines future battery technologies to discuss what materials should be taken into account in future recycling. In addition, a brief market outlook shows what quantities of the different lithium-ion battery technologies may be expected to be put on market and eventually in recycling. Finally, Chapter 4 discusses the consequences of the battery composition on the intermediate product of battery recycling, that is, black mass.

2. Lithium-ion batteries

The efficiency of a recycling process strongly depends on the feedstock which is treated. In this way, the composition of the feedstock must be carefully investigated, in this case, the lithium-ion battery. This chapter describes the composition of LIBs on two levels: on the battery pack level and the battery cell.

2.1 General composition of lithium-ion battery packs

Over the past years, batteries have been designed and produced for many different applications resulting in a great variety of geometries and sizes. LIBs in small devices, such as mobile phones and handheld machines, are relatively simple consisting of one or a small number of battery cells and do not require an extensive controlling system. However, LIBs for automotive applications are more complicated as a result of a large number of cells organized in several modules. A schematic picture of such a battery pack is shown in Figure 3 (left): the battery pack consists of several modules (yellow and orange) which are controlled by the battery management system (BMS) (green). The BMS controls and monitors voltage, temperature and current at a cell, module and battery pack level respectively. In addition, a large battery pack also requires a thermal management for safety, optimal performance and longevity. Moreover, such control systems require a large number of cables, containing copper and plastics and finally, for safe handling, a battery pack is protected from the environment and impact by a casing, generally made from aluminium or steel. (Latini et al., 2022)

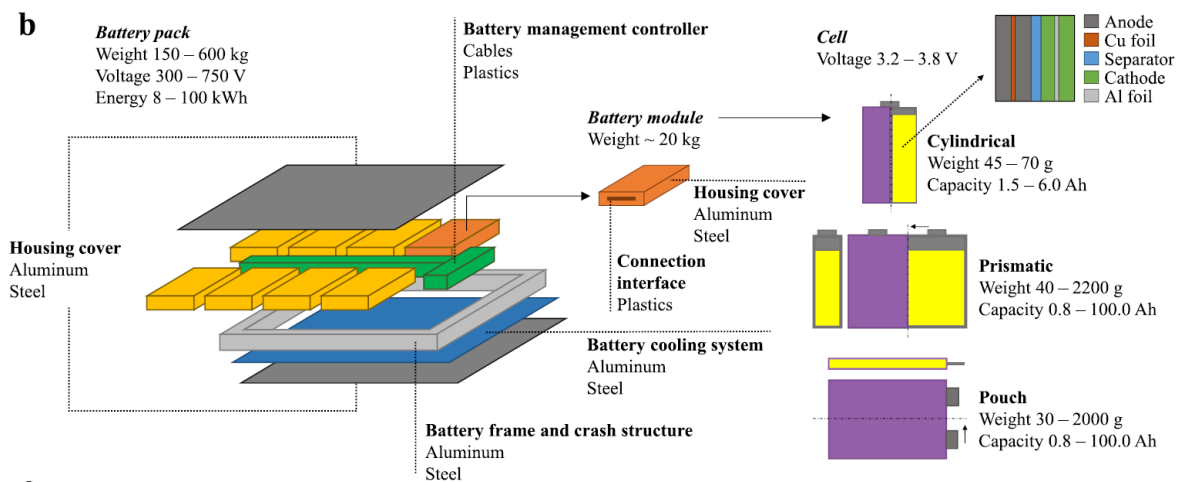


Figure 3: Schematic drawing of the arrangement of a typical battery pack : a battery pack consists of a number of modules, cables and electronics, such as the battery management system or controller. On the right, typical cell geometries are shown (top to bottom): cylindrical, prismatic and pouch. (Latini et al., 2022)

The most commonly used geometries of battery cells are cylindrical, prismatic and pouch, as shown in Figure 3 on the right. Cylindrical cells are employed in many LIBs as a result of cost-effective production and good mechanical stability. The components are wound into a jelly roll and packs with a steel case. The cells have a standardized sizes, as indicated by their names such as 18650 and 21700, but due to their shape, the packing density is lower than for prismatic and pouch cells. (Latini et al., 2022) The packing density has become more important for battery electric vehicles as the batteries become larger. However, as cylindrical cells are favourable in mass production, design of the battery pack and cooling system are crucial for automotive applications.

Similar to cylindrical cells, the components for prismatic cells are wound to create a jelly roll and compressed into a hard, rectangular casing. The shape of the cell facilitates maximum packing density and the flexibility of the dimensions provide additional advantages for several applications.

Pouch cells are similar to prismatic cells with respect to size and shape, however, the casing is quite different: it consists of a heat-sealable multilayer foil providing no or limited protection from internal or external events. In that way, additional safety measures need to be taken against risks due to gas production and related swelling of the cell, such as additional casing. (Latini et al., 2022) The hard casing of cylindrical and prismatic cells allows the presence of a safety vent which releases gases in a controlled way in case of too high internal pressure. However, pouch cells are attractive as a result of weight reduction, which has become an important aspect for the automotive industry.

For large battery packs from automotive or heavy duty applications, the materials of highest interest are present in the battery cells: all other materials are considered contaminants in the recycling process for cathode active materials (CAM). Components containing such non-CAM materials are manually dismantled if possible, examples of such materials are the battery pack casing and the BMS as indicated by the blue parts of the Battery System Periphery in the diagram of Figure 4.

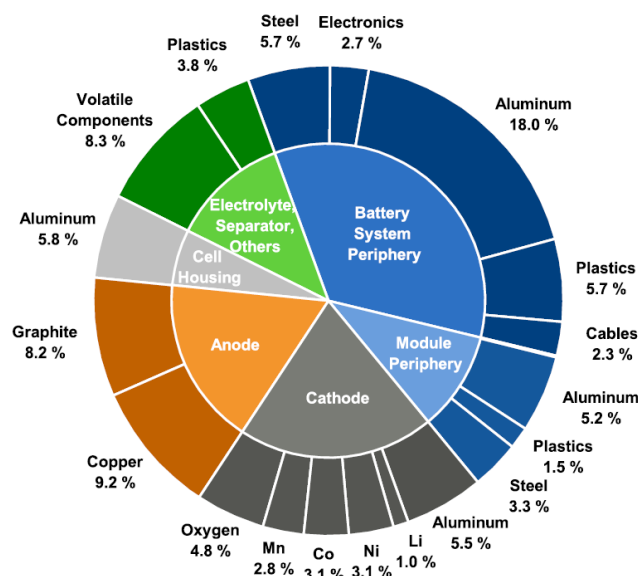


Figure 4: A generic composition of a lithium ion battery with a NMC111 chemistry. (Diekmann et al., 2017)

2.2 Materials for lithium-ion cell components

In addition to the BMS, cables and the casing of a battery pack, battery cells represent the major part of the weight of a battery pack.

In Figure 5 a schematic representation of a LIB is presented, showing the inner build-up of a basic battery cell with the standard elements that form a battery. Most LIBs are either wound up to a round cylindrical form or 'folded' in a somewhat flattened form, as is the case for prismatic or pouch cells. In the figure a cylindrical cell is presented, and the windings can be seen. Zooming in on the components from left to right: a current collector, generally an aluminium foil, the cathode consists of cathode active material, lithium metal oxides, to be described in more detail in 2.2, conductive carbon and a binder material, a separator membrane, preventing internal short circuits, but allowing transfer of ions; and the anode which consists of active anode material (intercalated graphite) with a polymer binder and finally another metallic current collector, generally a copper foil. The electrolyte (organic, to withstand the high voltages) is interspersed in the cathode, separator membrane and anode to support ion transfer. (Kim et al., 2021)

As most recycling technologies include a certain level of dismantling for high-quality recycling of electronics and aluminium, battery cells and, more specifically, their components determine the composition of black mass. This section will describe the separate components and their composition.

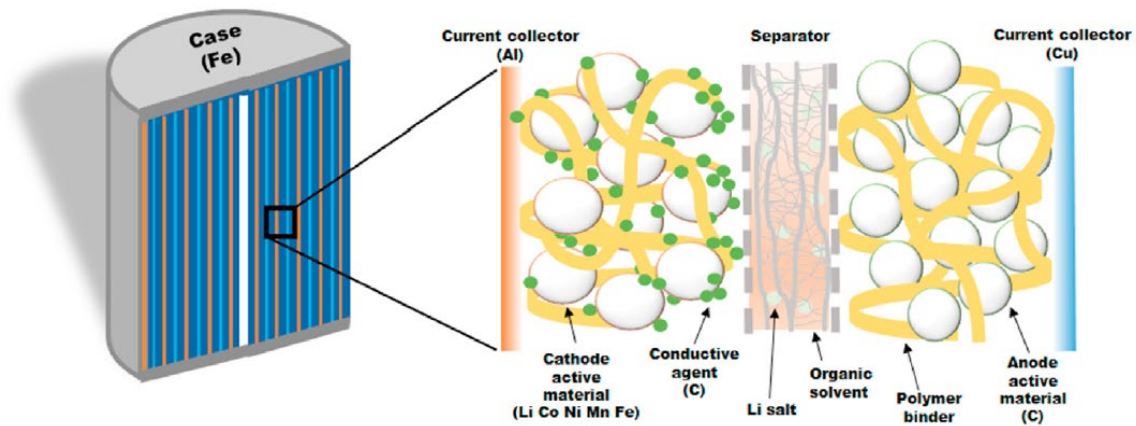


Figure 5: A schematic drawing of a cylindrical battery cell and its components. Copied from reference (Kim et al., 2021)

2.2.1 Cathode active materials

The cathode active material is the component of a battery cell that differs most. As LIBs have been introduced into the market in the 90’s for laptops and later for mobile phones, the application and requirements were very much different compared to the current applications of LIBs with corresponding requirements. In that way, the materials used for cell components in LIBs have developed to improve the overall battery performance, but more specifically for instance the energy density and cycle lifespan. Most developments impacting the cell composition were done on the cathode active materials. Figure 6 shows the most important cathode active materials with a comparison on the crucial properties and are described in more detail in the following subsections.

LIB cathode chemistries

	Ideal					Poor
Cathode types	LCO	LFP	LMO	NCA	NMC	
Chemical formula	$LiCoO_2$	$LiFePO_4$	$LiMn_2O_4$	$Li(Ni,Co,Al)O_2$	$LiNi_{0.33}Mn_{0.33}Co_{0.33}O_2$ (NMC111) $LiNi_{0.5}Mn_{0.3}Co_{0.2}O_2$ (NMC532) $LiNi_{0.6}Mn_{0.2}Co_{0.2}O_2$ (NMC622) $LiNi_{0.8}Mn_{0.1}Co_{0.1}O_2$ (NMC811)	
Structure	Layered	Olivine	Spinel	Layered	Layered	
Year introduced	1991	1996	1996	1999	2008	
Safety	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	
Energy density	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	
Power density	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	
Calendar lifespan	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	
Cycle lifespan	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	
Performance	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	
Cost	●●●●●	●●●●●	●●●●●	●●●●●	●●●●●	
Market share	Obsolete	Electric bikes, buses and large vehicles	Small	Steady	Growing (from NMC 111 > NMC 532 > NMC 622 > NMC 811 to no-cobalt chemistries)	

Figure 6: Schematic representation of various important properties of LIBs of the most common cathode chemistries. Source (Harper et al., 2019)

LCO – Lithium Cobalt Oxide

One of the first mature cathode chemistries has been the lithium cobalt oxide (LCO) chemistry and has led the market since the '90's, accounting for 63% of the worldwide battery sales. (Eshetu et al., 2021) The debut of LIBs gain attention in the market particularly with the growth of portable personal electronics. (Eshetu et al., 2021; Zhang et al., 2020) However, later on, alternative cathode active materials - such as NMC or NCA (currently more applicable to electric vehicles) - were developed due to the low natural abundance and consequently high cost of cobalt, as well as its toxicity.

The lithium and cobalt ions are well-ordered in a layered structure facilitated by the large size and charge differences. The optimal ordering results in an enhanced lithium-ion diffusion between the layers allowing high conductivity and fast charging rates. (Manthiram, 2020)

Batteries with an LCO cathode possess relatively high energy density, 150-190 Wh/kg, but relatively low capacity, on the order of 145 mAh/g. In addition, the LIBs last for 500 to 1000 full cycles, corresponding to the lifetime of a few years, making such batteries most attractive for portable electronics. (Latini et al., 2022)

A major drawback of LCO batteries is the thermal stability: this is relatively low and has proven to be an issue as thermal runaway, the self-accelerating event as a result of heat release and increasing temperature, is already possible at 150 °C. In that way, the LCO chemistry is not relevant for automotive applications for safety reasons. (Zubi et al., 2018)

The composition of LIBs with LCO cathode chemistry is relatively uncomplicated and has remained unchanged since introduction on the market: LiCoO_2 . In addition, the elements have different chemical properties, beneficial for efficient separation. Recycling of LCO containing LIBs is economically interesting as a result of the high concentration of cobalt.

LMO - Lithium Manganese Oxide

LIBs containing lithium manganese oxide based cathode active material (LiMn_2O_4) have a number of advantages due to the absence of cobalt: first, the material is relatively cheap as manganese is highly abundant. Second, the thermal stability of the material results in safer batteries, making them highly attractive for medical devices. (Zubi et al., 2018) In addition, the materials are relatively eco-friendly due to the non-toxic nature. The LMO cathode material has a high 3D structural stability allowing high electrical conductivity and fast lithium-ion diffusion, resulting in fast charge-discharge characteristics. (Manthiram, 2020)

On the other hand, LMO LIBs have a relatively low energy density, 100-150 Wh/kg, and low capacity, 120-148 mAh/g compared to other chemistries. (Houache et al., 2022; Latini et al., 2022)

However, in the presence of very low concentrations of H^+ ions, manganese dissolves in the electrolyte and shortens the lifetime of the battery. (Manthiram, 2020) As a result of these characteristics, LMO cathode active materials are often blended with NMC materials to combine the advantages of both chemistries: fast charging rate and high energy density. LMO-NMC blends are mostly used in automotive LIBs. (Houache et al., 2022)

LIBs containing LMO cathode active materials are not most attractive for recycling activities: due to the absence of cobalt and nickel, the value of recovered materials is low. However, when present in a battery waste stream, LMO based LIBs will most probably not disturb the recycling process as no additional or foreign contaminants are expected from LMO LIBs.

NMC – Lithium Nickel Manganese Cobalt Oxide

The NMC cathode material is a highly investigated cathode chemistry as a result of its excellent properties: relatively high capacity, high energy density and a high life cycle. The general formula of the material is $\text{Li}(\text{Ni}_x\text{Mn}_y\text{Co}_z)\text{O}_2$. However, in contrast with other cathode chemistries, a wide variety of compositions has been developed in order to further improve the performance. The Ni:Mn:Co ratio is

depicted in the chemistry name: NMC 111 or 333, NMC 523, NMC 622 and NMC 811. In addition, high cost for cobalt and poor labor conditions of mine workers has also been a driver for the limiting the cobalt concentration in the cathode active material. (Manthiram, 2020)

The NMC chemistry employs the best features of the elements: manganese contributes to a low internal resistance, nickel enables high capacity and cobalt yields a high conductivity and capacity. (Houache et al., 2022) [reference] However, an increasing concentration of nickel accelerates surface degradation of the cathode layer as a result of unstable Ni^{4+} ions transforming into a stable NiO phase, leading to a capacity decay, as depicted in Figure 7 (left). As a result of the presence of Ni^{4+} ions, the electrolyte decomposes at the cathode surface. Finally, high nickel content leads to structural instability resulting in thermal safety challenges also shown in Figure 7 (right). (Houache et al., 2022; Yoon et al., 2017)

In conclusion, LIBs containing NMC cathode active materials may strongly vary in composition with respect to nickel, manganese and cobalt. Most LIBs becoming available for recycling on the short term will have similar concentration of the three elements, however, nickel will become predominant for later generations of NMC LIBs.

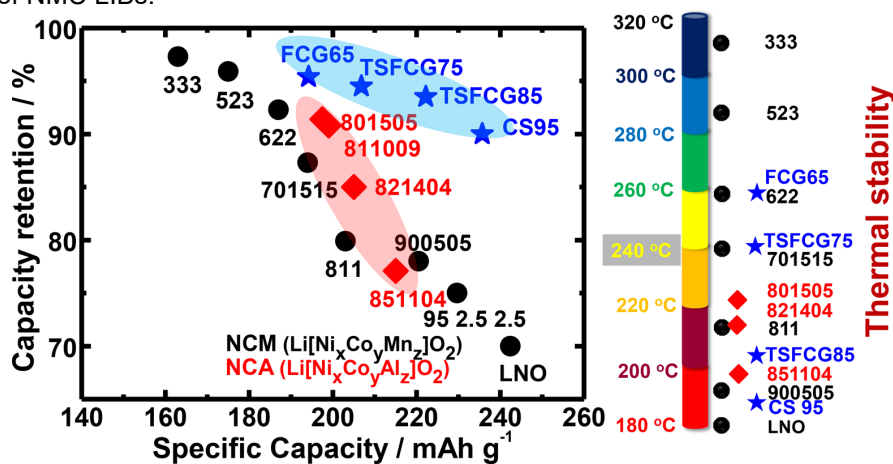


Figure 7: Capacity as a function of capacity, thus cycling stability, by altering the molecular ratio for NMC and NCA cathode active materials (left) and experimental results using differential scanning calorimetry (DSC) on the thermal stability of cathode active materials. (Yoon et al., 2017)

NCA - Lithium Nickel Cobalt Aluminium Oxide

Most batteries containing NCA cathode active material have the following formula: $Li(Ni_{0.8}Co_{0.15}Al_{0.05})O_2$. As a result of high capacity, 180-200 mAh g⁻¹, and very high energy density, up to 260 Wh kg⁻¹, NCA containing LIBs are very attractive for automotive applications. (Latini et al., 2022) Similar to NMC LIBs, the molecular ratio of Ni:Co:Al is altered to reduce costs and improve performance. However, the consequences are comparable: with increasing concentration of nickel, a relatively faster capacity decay is observed and the thermal stability is significantly lowered as shown in Figure 7. (Yoon et al., 2017)

In terms of recycling, NCA cathode active materials are similar to the NMC chemistry, however, the relatively low amount of aluminium can be considered a contaminant as none of the other cathode chemistries contain aluminium. In this way, NCA LIBs are preferably not fed to any recycling process designed for treatment of regular nickel and cobalt containing LIBs.

LFP - Lithium Iron Phosphate

Lithium iron phosphate, $LiFePO_4$, LIBs have gained much attention as a result of their advantages: since the chemistry type does not contain any cobalt or nickel, similar to LMO batteries, production costs below \$100 per kWh are made possible. (Yang et al., 2021) In addition, due to the structural stability, LFP batteries also show an improved thermal stability, and inherently improved safety. In addition, the high structural stability results in long cycle life, up to 2000 cycles. (Houache et al., 2022; Latini et al.,

2022) However, the LFP cathode chemistry is characterized by a low energy density, 90-120 Wh/kg, but relatively high capacity, 150-170 mAh/g, making them most applicable for larger applications, such as energy storage systems and heavy duty applications. (Latini et al., 2022)

LFP containing LIBs have a fixed chemistry of the cathode active material: LiFePO_4 . Similar to the LCO cathode chemistry, the composition has not been altered and the composition of LIBs with a LFP cathode chemistry is relatively straightforward. However, this will not be the case for recycling of such LIBs as a result of the low value of the primary raw materials and thus also the recycled materials. In addition, when mixed with cobalt-based batteries, a hydrometallurgical recycling process will be greatly hindered by the contamination of iron and phosphate and should therefore follow a separate recycling route. This will also be discussed in Deliverable 6.2.1 of the project.

2.2.2 Anode active materials

Most of LIB anodes are carbon based materials, such as graphite and graphene. Graphite materials can be obtained both synthetically and from primary sources. They are cost-effective, long lasting, porous and they meet voltage requirements of most commercial LIBs.

The anode material accounts for 20% of the entire battery weight. Therefore, a large amount of spent graphite is generated every year, due to end-of-life batteries. (Costa et al., 2019)

However, graphite anodes have a lack of high capacities. To improve this deficit, silicon oxide (SiO_x) is sometimes added to the graphite anode in small amounts (2-10%). This is based on the fact that Si and SiO_x have a fivefold-tenfold higher energy densities. Other types of additives, such as polymer and graphene coatings, have also been under study to enhance coulombic efficiencies. These additives allow the use of higher Si quantities. Nevertheless, Si carries a large volume expansion as a consequence of its higher capacity, thus affecting the stability of the solid-electrolyte interface (SEI). Moreover, Si expansion may cause mechanical grinding on graphite. Therefore, safety concerns still remain when it comes to adding Si to graphite anodes. Furthermore, anodes made of lithium titanate (LTO) are also commercially accessible, though with modest market applications, due to issues related to safety, relatively low energy density and limitations to operate over a wide temperature window. (*Anode materials for Li-ion battery manufacturers*; Grey & Hall, 2020)

2.2.3 Other components

Current collectors

The function of current collectors consists of collecting the electrical current produced at the electrodes and connecting with external circuits. The current collectors are usually foils made from aluminum (Al) and copper (Cu) for cathodes and anodes, respectively. Both current collectors achieve almost a 15% of the total weight of a battery as is shown in **Figure 4**. (Diekmann et al., 2017)

Current collectors can be found as foil, foam, mesh, etched and coated with for example carbon, graphene oxide, manganese and aluminum oxide composite and chromate coatings. The differences between all these structures may have an impact on the battery's capacity. For instance, in the case of Al collectors, coatings are quite effective to improve their conductivity for a better electrode performance. For example, in case of LiFePO_4 cathodes with a carbon-coated Al current collector compared to a bare aluminum collector, the discharge capacity can be increased from 140 to 160 mAh/g at a low current rate of 0.2C, and the capacity retention is enhanced from 15% to 70% at a high current rate of 5C. Moreover, coating thickness should be controlled. Though thick coatings may add extra weight to the battery, thin coatings may turn into insufficient protection and conduction. Therefore, it is important to find the right balance without compromising the efficiency of the coating.

Other type of coatings may also be found, such as Mn and Al oxide composite, graphene oxide, chromate and graphene, among others. (Zhu et al., 2021)

Figure 8 summarizes the structures that can be found in LIBs current collectors, as well as their main differences in physical properties, according to their composition.

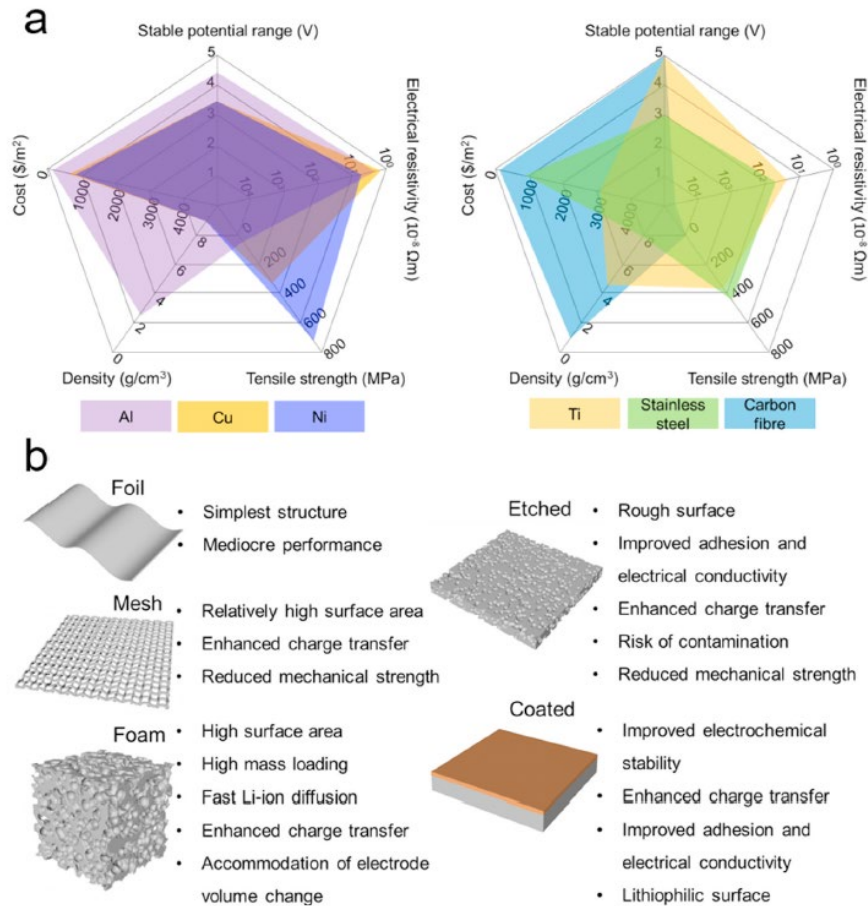


Figure 8: a. Comparison of physical properties and cost of Al, Cu, Ni, Ti, stainless steel and carbon fibre current collectors; b. most relevant advantages and disadvantages of five current collectors structures. (Zhu et al., 2021)

Another relevant function of the current collector is serving as a mechanical support for the electrode. In order to improve the integrity of the electrodes as well as the adhesion between electrode active materials and current collectors, a polymeric binder (i.e., polyvinylidene difluoride (PVDF)) is added for this purpose.

Since current collectors are non-active materials, reducing their thickness turns into an advantage in terms of reducing the battery's weight and, at the same time, increasing its energy density. Figure 9 depicts the progress on the development of current collectors for LIBs and, particularly, how their thickness was reduced over the past decades. For recycling this means that old LIBs will yield higher quantities of current collectors in the black mass production process.

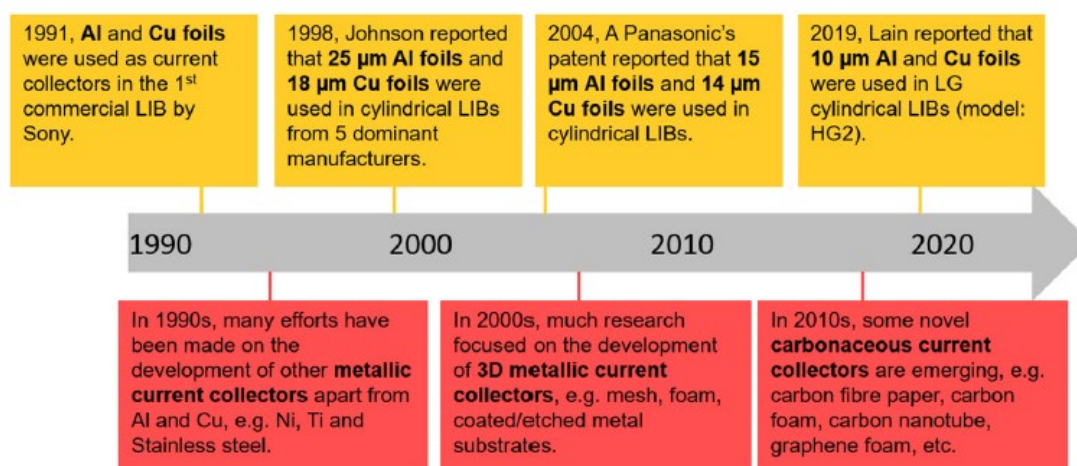


Figure 9: Development of current collectors for LIBs, through the past decades (industry: yellow; academia: red). (Zhu et al., 2021)

Nickel (Ni), titanium (Ti), stainless steel and carbon fiber are part of the list of market current collectors, and can also be commercialized in any of the above structures. Nevertheless, the market share is smaller than that of Cu and Al current collectors, so it is expected that most of spent LIBs will have Cu and Al based current collectors.

With regards to recyclability of current collectors, Al and Cu foils are reported to be easily separated from electrodes by means of ultrasonic treatment or heating, for further reuse or recycle. (He et al., 2015; Or et al., 2020)

To summarize, the composition, the thickness and the structure of the current collector may indeed have an impact in the resulting composition of the black mass.

Separator

The main objective of the separators is to facilitate the transport of ions, in this case, lithium ions. The followings are the most important characteristics of separators: (Costa et al., 2019)

- Permeability: high permeability leads to a better ionic transport between electrodes;
- Porosity or pore size: should be above 50% for a good battery performance, avoiding the loss of mechanical integrity, which would affect battery safety;
- Electrolyte absorption and retention: high absorption is also related to a good ionic transport;
- Wetting ability: determines the internal resistance of the battery and therefore the life cycle. High wettability gives rise to a better ionic transport and an improved interfacial compatibility between the electrodes and the separator, thus leading to a better cycle performance.
- Chemical, mechanical and thermal stability: they all have an impact in long term operations. For instance, thermal stability is relevant to avoid melting at higher temperatures and, therefore, destruction of the structure, in case of polymer separator membranes.

Battery separators are usually made of a porous membrane embedded in a liquid electrolytic solution. The membranes are most commonly made of polymeric or ceramic based materials.

The existing separator membranes made of polymeric materials can be found as microporous, nonwoven and electrospun membranes. Moreover, composite and polymer blends membranes can also be found in batteries, as well as membranes with external surface modifications.

Among these categories, microporous, composites and polymer blends membranes are the most common separator membranes found in LIBs.

Table 1 lists the different polymer compositions that can be present in microporous membranes.

Table 1. Polymer compositions present in microporous type separator membranes. (Costa et al., 2019)

Materials	Electrolyte solution	Conductivity (mS.cm ⁻¹) and capacity (mAh.g ⁻¹)	Anode/cathode	Main achievement
PP	1 M LiPF ₆ in EC:DMC	0.16; 141 (0.1C)	Li metal/LiCoO ₂	Increase degree of porosity
PVDF-CTFE	1 M LiTFSI in PC	1.5; 92 (2C)	Li metal/LiFePO ₄	Good cyclability and rate capability
PVDF	1 M LiPF ₆ in EC:DMC:DEC	1.72; 110.3 (5C)	Li metal/LiFePO ₄	Higher electrolyte uptake and improved uptake rate
PVDF-HFP	1 M LiPF ₆ in EC:DMC	0.36–4; –62 (C/5 at 55 °C)	Li metal/LiMn ₂ O ₄	Improved high temperature cycling performance
PVDF-HFP	–	1.08; 175 at 110 °C	Li metal/ Li(Ni _{0.8} Co _{0.1} Mn _{0.1})O ₂	Efficient migration of electrolyte salts
PVA	1 M LiPF ₆ in EC:DEC (1:1, v/v)	1.20; 84.3 (4C)	Li metal/LiFePO ₄	Improved electrochemical performance
Cellulose	1 M LiClO ₄ in EC:DEC (1:1, v/v)	–0.8; 100 (1C)	Graphite/LiFePO ₄	High porosity, wettability and mechanical robustness
PI	1 M LiPF ₆ in EC:DMC:EMC	2.15; 110.4 (0.5C)	Graphite/LiCoO ₂	High discharge capacity and better rate capability
PAEK	1 M LiPF ₆ in EC/DEC/EMC (1:1:1, v/v/v)	1.99; 121 (C)	Li metal/LiCoO ₂	Improved liquid electrolyte holding capacity than PP membranes
Polybenzoxazole	1 M LiPF ₆ in EC/DEC (1:1, v/v)	–103 (1C)	Graphite/LiCoO ₂	High power density
Cladophora cellulose	1 M LiPF ₆ in EC: DEC (1/1, v/v)	0.4; 135 (0.2C)	Li metal/LiFePO ₄	Thermally stable at 150 °C and electrochemically inert between 0 and 5 V vs. Li+/Li.
Poly(m-phenylene isophthalamide) (PMLA)	1 M LiPF ₆ in EC/DMC/EMC (1:1:1, wt/wt/wt)	1.5; 108.7 (0.5C)	Graphite/LiCoO ₂	High-heat resistance and high-power density lithium-ion batteries
PI	1 M LiPF ₆ in EC: DEC (1/1, v/v)	–	Li metal/LiFePO ₄	Early alarms of Li penetration
PPTA	1 M LiPF ₆ in EC: DEC (1/1, v/v)	0.21; –110 (C)	Graphite/LiCoO ₂	Good electrolyte wettability, excellent mechanical properties, and superior thermal stability
PEEK	1 M LiPF ₆ in EC/DMC/EMC (1:1:1, v/v/v)	0.11; 124.1 (5C)	Li metal/LiFePO ₄	High thermal stability and good rate capability
OHPEEK	1 M LiPF ₆ in EC/DME	–; 90 (4C)	Li metal/ LiNi _{0.5} Mn _{0.2} Co _{0.3} O ₂	High anti-shrinkage property and high thermal stability
PI	1 M LiPF ₆ in EC/DEC (1:2, v/v)	–; 125.3 (0.1C)	Li metal/LiCoPO ₄	Improved coulombic efficiency and capacity retention
PBI	1 M LiPF ₆ in EC/DMC/EMC (1:1:1, v/v/v)	0.13; 154.5 (0.2C)	Li metal/LiFePO ₄	High thermal stability and electrolyte wettability
OPBI	1 M LiPF ₆ in EC/DEC (1:1, v/v)	1.03; 160 (0.1C)	Li metal/LiFePO ₄	Only ~5% thermal shrinkage after heating at 200 °C for 1 h and good fire-retardant properties
Cladophora cellulose	1 M LiPF ₆ in EC: DEC (1/1, v/v)	0.82; 125 (C)	Li metal/LiFePO ₄	Enhanced battery performance, particularly at higher cycling rates
PPC	–	0.22; 140 (0.1C)	Li metal/LiFePO ₄	Excellent electrochemical stability at ambient temperature
PVA	1 M LiPF ₆ in EC: DEC (1/1, v/v)	1.41; –140 (0.5C)	Li metal/LiFePO ₄	Improved safety and matched electrochemical performance.

The materials of the separator membrane may vary depending on the battery's chemistry (i.e. cathode and anode composition).

Though many research has been performed and there are plenty of existing membrane type separators, the microporous membrane as well as the microporous membrane with ceramic coating are currently the best options for industrial applications.

Electrolyte

For typical LIBs, the electrolyte solution consists of a lithium salt dissolved in an organic solvent. Table 2 lists the most common lithium salts that can be found in the electrolyte solution.

The main relevant properties of the solvent should be a high fluidity as well as a high dielectric constant. In that way, organic solvents, such as dimethyl carbonate and ethylene carbonate, are suitable candidates for LIB applications. (Costa et al., 2019)

Overall, the electrolyte should meet several requirements, such as low vapor pressure, high ionic conductivity and large electro-chemical stability.

Table 2. Commonly used lithium salts found in LIBs. Melting temperature and their advantages and disadvantages. (Costa et al., 2019)

Lithium salt	Melting temperature (°C)	Advantages	Disadvantages
LiClO ₄	236	Low cost, Moderate ionic conductivity	Dangerous, Explosive
LiPF ₆	200	High ionic conductivity	Very hygroscopic, Thermally unstable
LiAsF ₆	300	High ionic conductivity	Toxic
LiCF ₃ SO ₃		Good thermal stability, Non-toxic	Low ionic conductivity
Li(CF ₃ SO ₂) ₂ N	234	High ionic conductivity, Good electrochemical stability, Non-toxic	High cost

Taking into consideration the safety concerns regarding the most conventional electrolytes, ionic liquids (ILs) are a good alternative to replace them. They are chemically and electrochemically stable, non-flammables, they have a high ionic conductivity and low vapor pressures and they are considered green solvents. Suitable ILs for LIBs could be quaternary ammonium cations, such as imidazolium and pyrrolidinium, combined with inorganic or organic anions (e.g., PF₆, BF₄, perfluoroalkylsulfonylimide, among others). Nevertheless, there is still more work to be done to demonstrate the feasibility of replacing conventional electrolytes by ILs. (Costa et al., 2019)

Binder

In order to adhere cathode and anode active materials onto the surface of the current collectors, an organic compound is added to act as a binder. The following features are some of the technical properties that should be met by binders:

- Adhesion: a binder layer thickness of 5-10 nm represents a good balance between sufficient adhesion and maximized active material content.
- Dissolution properties: soluble in non-aqueous solvents for a homogeneous distribution within the active material;

PVDF is one of the most commonly used binders due to its good physic-chemical and mechanical properties. (Zhong et al., 2021) Figure 10 shows a scheme of the possible binding mechanisms of PVDF in LIBs, based on simulation calculations by density function theory (DFT).

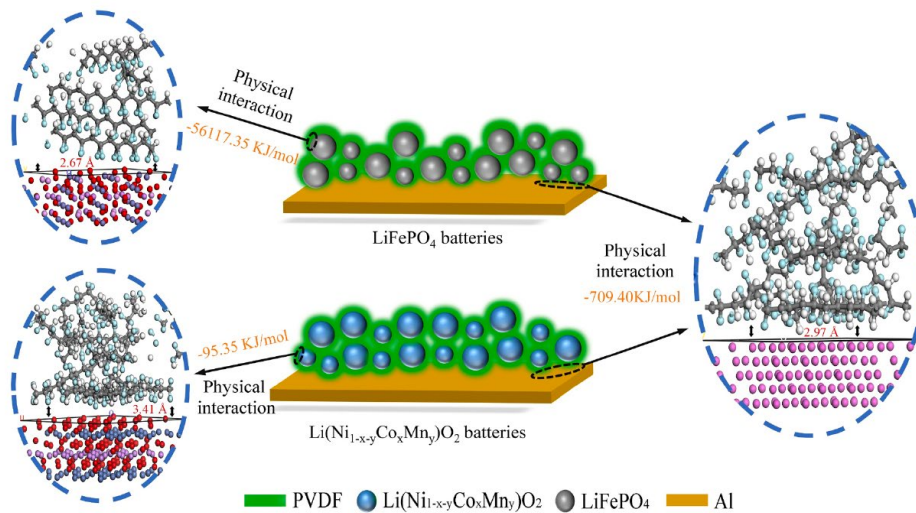


Figure 10: Scheme of potential binding mechanisms of PVDF contained in LIBs. (Zhong et al., 2021)

As can be seen, the binding mechanism of PVDF with both cathode active materials and current collectors could be explained by physical interactions. This is also in agreement with Auger Electron Spectroscopy (AES) analyses, which indicates that there are no chemical bonds among the surfaces of cathode active materials, PVDF, and current collectors, such as Al. This is relevant when designing recovery routes of LIBs materials.

Nonetheless, removal of PVDF is not straightforward, besides the fact that it also carries safety concerns, such as the release of hydrogen fluoride (HF) - as a byproduct from pyrolysis -, or its removal by dissolution, making use of highly toxic organic solvents, such as N-methyl-2-pyrrolidone (NMP) or dimethylformamide (DMF). Usually, the polymer binder ranges between 2-8% of the electrode's weight%. (Miranda et al., 2019)

Therefore, battery manufacturers are diverging from fluorinated binders to alternative options, such as carboxymethyl cellulose (CMC) (water soluble), as well as styrene butadiene rubber (SBR), both for anodes active materials. (Harper et al., 2019)

In literature, it is possible to find studies focused in the use of cellulose, lignin and guar gum based binders, though these developments are still at low TRL. (Nirmale et al., 2017)

3. Outlook on lithium-ion battery developments for mobile applications

At present there is a considerable effort in R&D to arrive at better batteries with higher specific energy and or specific power. The Dutch (emeritus) professor Peter Notten noted a couple of years ago that given the present development, most likely next steps in power storage will be several: an ‘upgrade’ in lithium ion technology by introducing solid state electrolytes, the introduction of sodium-ion batteries (watery electrolyte), and further down the road the introduction of lithium-sulphur and metal air batteries, see also **Figure 11**. (Verheij & Bolech, 2017) In this chapter we will briefly describe what the technologies stand for, and particularly what they mean for materials recycling from Li-ion batteries.

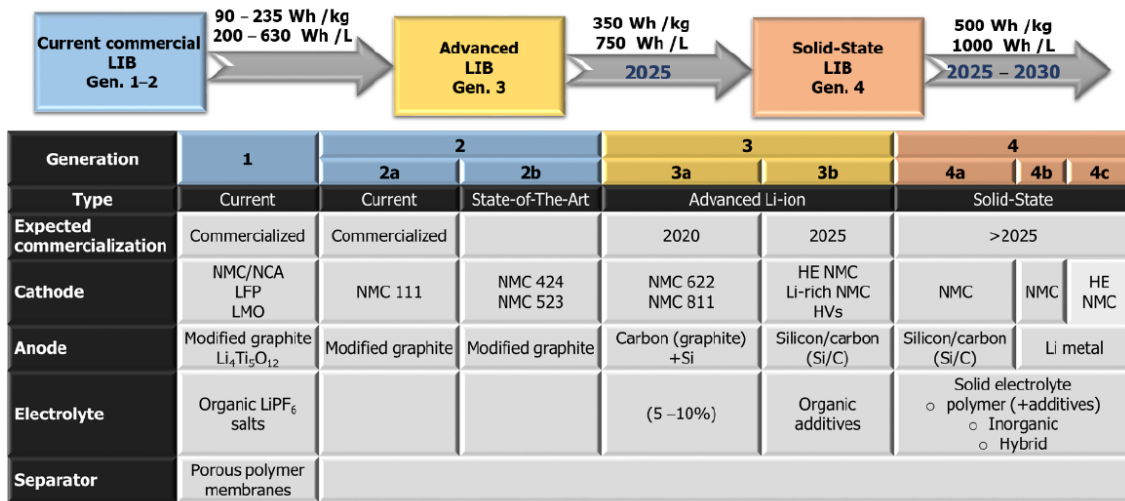


Figure 11: A schematic of current and future battery technologies. Copied from reference (Houache et al., 2022).

3.1 Developments in lithium-ion battery technologies

3.1.1 Lithium ion batteries with altered anode composition

Silicon

The carbon used in present LIBs can be partially exchanged by silicon. That way the ion-absorbing capacity (good for energy density of the battery) can be improved a lot. However, the long term stability of the material (good for life-time expectancy) decreases because of higher volume expansion of silicon during intercalation (the uptake of ions in the materials crystal lattice) and lower resilience of the material compared with that of graphite. Two Dutch companies are actually developing anodes with silicon in it: Leyden Jar is developing silicon containing anodes, and Delft Imp (for “Intensified Material Production”) enhances anodes with a silicon coating.

Nano carbon

Apart from adding silicon, also carbon anodes with higher permeability can improve battery performance. As an example, the French company Nawa produces batteries with nano carbon in it. The nano-structured electrode has very large specific surface area (and hence good current carrying capability).

Lithium Titanate

A special category in “altered” anode compositions is formed by the Lithium Titanate cell chemistry (LTO), and an enhanced version thereof using Lithium Niobium Titanate (NTO). This type of LIB has as a special feature a thin layer of fine needle-like lithium titanate crystals on the anodes. As a result the

anode can handle relatively high current density, compared to anodes without such a layer. This makes this type of battery particularly interesting for high power applications. The capacity of the cells is much lower than that of the types typically used in electric vehicles. On the other hand this type of cell can survive many more cycles than a NMC cell. Typically 10,000 up to 15,000 life time cycles for lithium titanate compared to 2500 up to 3500 cycles for “high energy” LIBs. Lithium titanate batteries are mostly used in very specific (high power) functions. As such it will only serve a small fraction of the total LIB market, and is not likely to form a large portion of LIBs to be recycled.

With regard to recycling of cathode materials, little changes. The chemistry of the cathode is similar to the currently produced LIBs. Therefore the same hydrometallurgical recycling technology for conventional LIBs will be useful for these alternative types as well.

Alloy anodes

Currently, alloy anodes - combining Aluminum (Al), Tin (Sn), Magnesium (Mg), Silver (Ag), Antimony (Sb), among others - are being studied as potential substituents of carbon anodes. Alloy anodes are known due to its two-to-ten times higher specific capacity than the one of anodes made of carbon material. Some alloy anodes combine C and metals. As an example, Mao and Dahn *et. al.* synthesized an alloy powder of Sn-Fe-C. This alloy combines two phases: SnFe_3C (the inert matrix) and Sn_2Fe (the active phase). (Mao & Dahn, 1999) When the composite is made of 25% of Sn_2Fe and 75% of SnFe_3C , the battery displays high reversible capacities as well as good cyclability. (Nzereogu *et al.*, 2022) Nevertheless, these active materials are not yet at market level.

3.1.2 Solid state batteries

The working principle behind solid state is the same as in conventional LIBs. The difference is that liquid electrolyte and the separator foil are exchanged for a solid conductive material like lithium phosphorus oxynitride or polymer electrolytes. This provides much better mechanical stability to the battery compared to liquid electrolyte batteries. The conductivity of the solid electrolyte (actually transport-paths for ions moving through the electrolyte) is however much lower than it is in a conventional liquid electrolyte, and interfacing with the solid electrolyte suffers from constriction resistance. Fortunately the difference can (partly) be compensated by reducing the thickness of the solid layer (often deposited by sputtering a thin layer). Solid state batteries are already available on the market (although numbers as well as battery sizes are still relatively small), for example from companies Quantum Scape and Store Dot.

In Figure 12, a graphic explanation is provided how the a new design of solid state batteries by LionVolt (a spin-out from TNO) combines two favourable characteristics in one product: high energy density and at the same time fast charging (i.e. high power density). The special characteristic is the 3D structure with nano-pillars that drastically increase the active surface of the electrodes, so that high energy density and high power density can be realised in the same device. Given the improved safety compared to present day LIBs, mainly due to the omission of flammable liquids as electrolyte, this type of battery presents a remarkable combination of higher performance and at the same time improved stability and safety.

With regard to recycling of materials, the mechanical pre-treatment of solid state batteries may require a somewhat different approach compared to that for present day batteries. The higher mechanical stability (approaching a ‘monolithic’ construction) may be somewhat harder to shred. On the other hand, once the cells have been shredded and the materials inside have become accessible, the relatively thin layer of solid electrolyte can probably be removed or dissolved without difficulties. Further, the chemistry of the electrodes is no different from that in ‘standard’ cells, though, so that basic techniques for hydro-metallurgical recycling of standard Li-ion batteries will remain of service for the newer solid state versions.

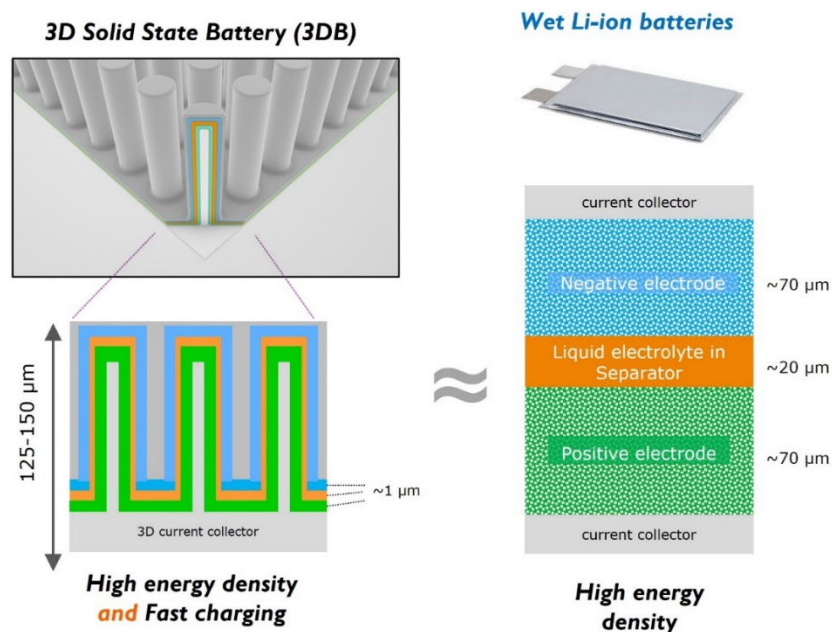


Figure 12: Schematic drawing of LionVolt's 3D solid state Li-ion Battery, explaining the combination of two favourable characteristics that without solid state was hard to reach. (Unnikrishnan, 2019)

3.1.3 Metal-air batteries

Metal-air batteries are actually fuel cells in which the fuel is a metal. A major advantage is the high energy density, and very easy storage of the fuel. Because of its solid state, no cooling or pressurising of the fuel is necessary and with adequate design shelf life can be very long. (Giffin, 2016) At present primary (i.e. non-rechargeable) metal air batteries are in widespread use already. For example, zinc-air batteries are popular for powering hearing aids and comparable light-weight applications. The much higher specific energy that could be reached by these batteries holds a great promise, but this is counteracted by no or very limited possibility to recharge the batteries. Technology to reclaim elements from Lithium-ion batteries may very well be useful for (future) recycling efforts on metal-air batteries. At this point most of such ideas are speculative, though.

With regard to recycling of materials, metal-air batteries are quite different, and not likely to fit in the hydrometallurgical recycling process for present LIBs. The chemistries are too different. However, the oxygen-intaking-electrode (cathode during discharge) may consist of manganese oxide so that for certain types of this kind of battery, the same hydrometallurgical recycling routes may be useful. Also hydrometallurgical processes may be adapted to also process input streams from metal air batteries. Overall the infrastructure required for LIB recycling may at some point in future be adjusted to also digest solid metal fuel cells.

3.1.4 Sodium-ion batteries

Sodium-ion batteries are an upcoming technology with low energy density, but are made from cheaper feedstock materials and with much reduced safety risks compared to LIBs. The cathode materials used in LIBs can equally well be used for the cathodes in sodium-ion batteries, however a broad variety of cathode materials, with and without dopants, are being investigated. (Lyu et al., 2019) Sodium-ion batteries are an upcoming technology with a somewhat lower energy density. Because of the growing demand for energy storage systems (ESS) in a sustainable power supply (with intermittent generators) this type of battery may become very important for small and medium scale buffering of wind or solar energy. Reduced price and inherent safety (water based chemistry) make it an attractive option (see for example Greenrock). (BlueSkyEnergies, 2020) Since the electrode materials are to some extent

comparable to those for lithium ion batteries, this means that recovery and recycling technology for Li-ion can be adjusted for sodium-ion batteries as well. Important to note is that cathode materials for sodium-ion batteries are often more complex compared to lithium-ion batteries, as they contain more different metals, which may be a challenge to overcome when adjusting the recycling process. In future production, lower quality electrode materials might be used for Na-ion, whereas top-quality materials flow into the highest quality LIBs. For the production of Na-ion batteries, requirements may be less strict than for high-performance high-power automotive batteries. For use in sodium ion batteries, it will probably be acceptable to use 2nd grade electrode materials from battery recycling process, or have more relaxed purification requirements (also resulting in a somewhat lower materials grade).

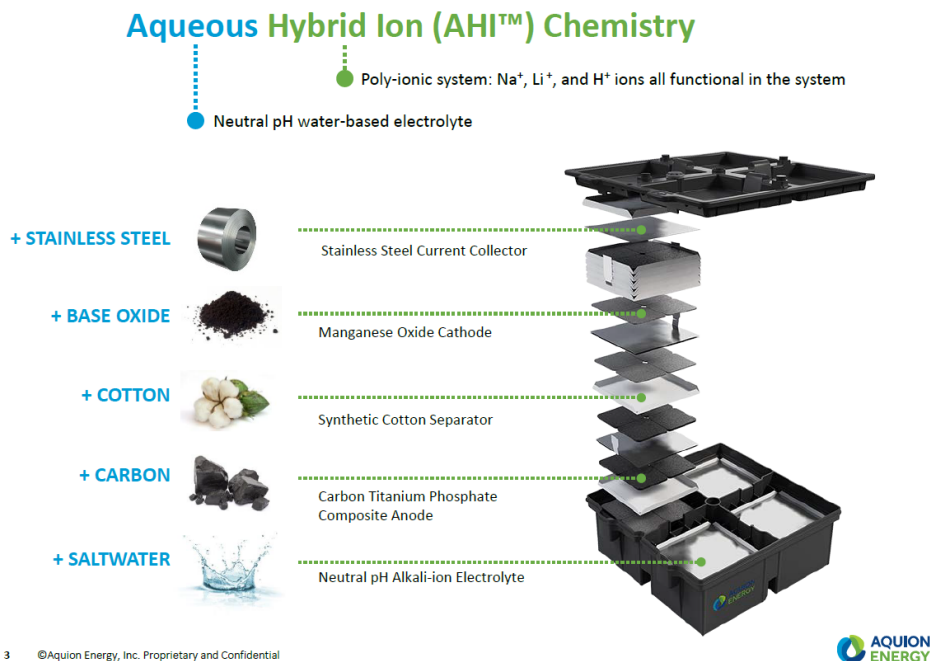


Figure 13: Schematic drawing of Aquion Energy's Salt water battery. (*Clean energy systems need clean batteries*, 2016)

3.2 Market outlook

Various consultancy firms have investigated the markets for LIBs and monitor the markets shares of manufacturers as well as cell chemistries. Presently, the majority of LIBs are in a relatively early stage of their expected life times, and at the same time the production of LIBs is growing every year. Consultancy firms have also executed studies into battery compositions expected to be used in new electric vehicles (as well as other battery machinery) in years to come. As an example the findings of a 2018 study by McKinsey is presented in Figure 14. This study focused solely on electric vehicles and clearly shows a trend away from LFP (then popular in China, the dominant car market of the world) and a decrease (rest of the world) of Tesla's market share, leading to a smaller fraction of NCA in the battery market projections.

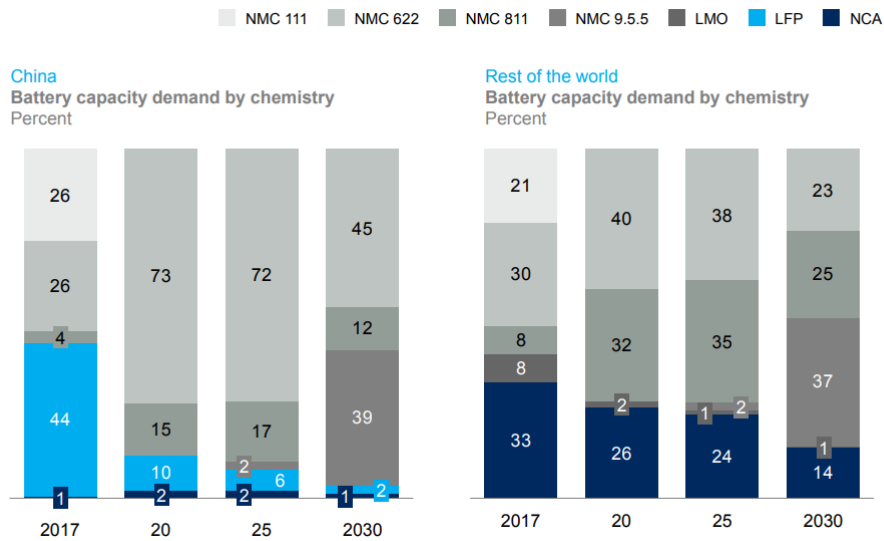


Figure 14: Distribution of Electric Vehicle Batteries by particular chemistry (other battery demand segments were excluded in this study). (*Basic Materials Institute’s battery raw materials demand model, 2018*)

While the electric vehicle market is definitely an important driver for developments, other fractions of the LIB market are substantial as well. This can be seen in Figure 15.

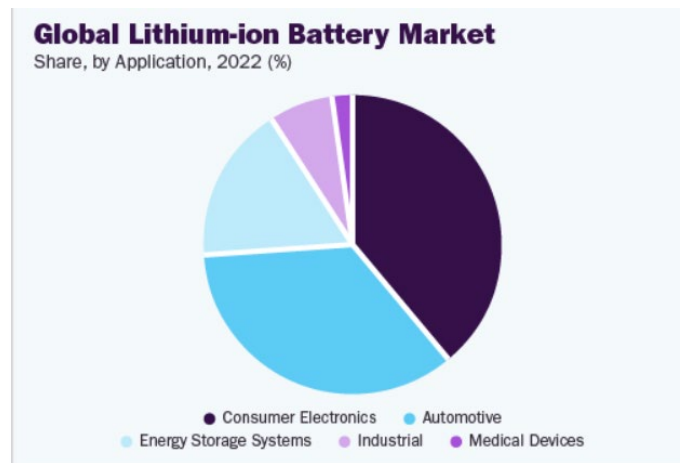


Figure 15: The lithium-ion battery market by sector. (GrandViewResearch, 2022) The shares are given based on value. In volume (relevant for recycling), automotive and particularly energy storage claim larger shares.

In a 2021 study it was shown that for many applications slightly lower specs than for high-end passenger car applications can be good enough or even preferable. (Yang et al., 2021) In recent years the further development of LFP technology with enhanced chemistry as well as stacking density has even led to the “mediocre” LFP becoming really competitive compared to other chemistries. This is illustrated in Figure 16. It can be seen that the improved LFP batteries from BYD in their newly developed ‘blade’ geometry, are competitive in specific energy as well as energy density compared to even top-tier products (despite the basic cathode material performing having lower performance than the state of the art LIBs). It is worthwhile to note that this insight contrasts somewhat with the predictions in the McKinsey study cited in Figure 16.

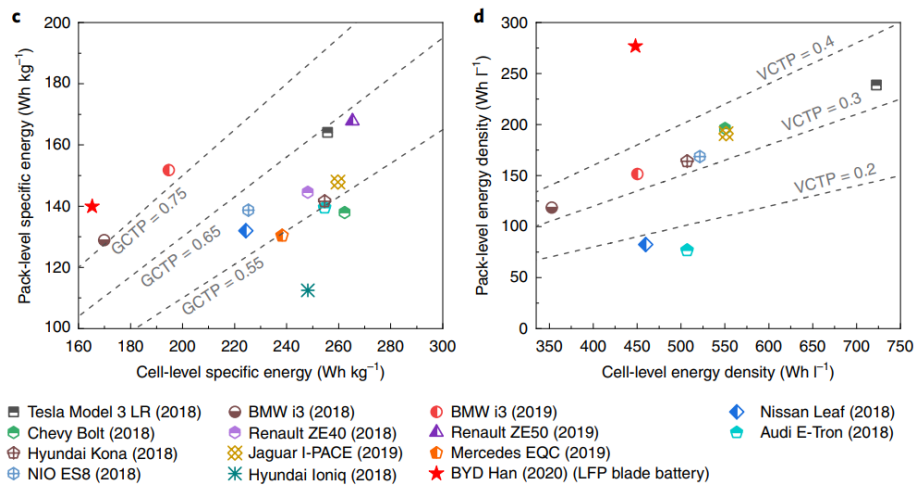


Figure 16: Despite moderate basic properties of LFP chemistry, advanced designs can still produce quite attractive LiB's based on LFP. The “BYD Han” data points (red star) use LFP. (Yang et al., 2021)

Overall, looking at the total battery market a study by Roskill tells another story, that may reflect developments more accurately. (Merriman, 2020) The outcome of that study is captured in Figure 17. There it can be seen that there are two trends in the LIB market: chemistry is trending toward ever lower cobalt and manganese content, and LFP, thus without cobalt or manganese, is capturing a growing share of the markets.

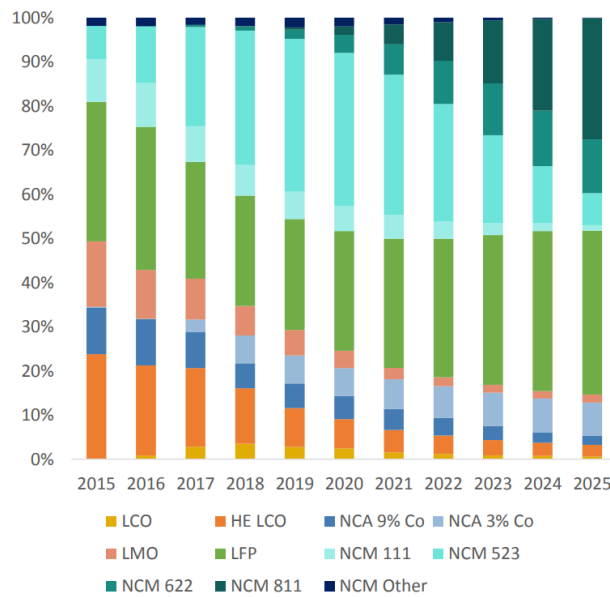


Figure 17: Cathode usage by type (% market share 2015-2025), based on sales figures and knowledgeable predictions. (Merriman, 2020)

The growth of the overall market as well as the (much sharper) growth in nickel content, Figure 18, still point at significant increase in demand for the most critical elements in (high-quality) LIB applications. These predicted sharp increases in demand make it all the more interesting to look into possibilities for re-covering, re-using and re- or upcycling materials from end-of life LIBs. Presently, recycling LFP may not be economically attractive, but its market share will grow and perhaps become dominant. This still makes it interesting to look into lithium and iron recovery from spent batteries, all the more because EU legislation mandates certain fractions of the batteries' ingredients to be sourced from recycling (e.g. for

Cobalt $\geq 12\%$ in 2030, and $\geq 20\%$ 2035). (EC, 2020) Even though this may not be economically feasible now, sheer volumes end-of-life LFP batteries are expected in a decade or so.

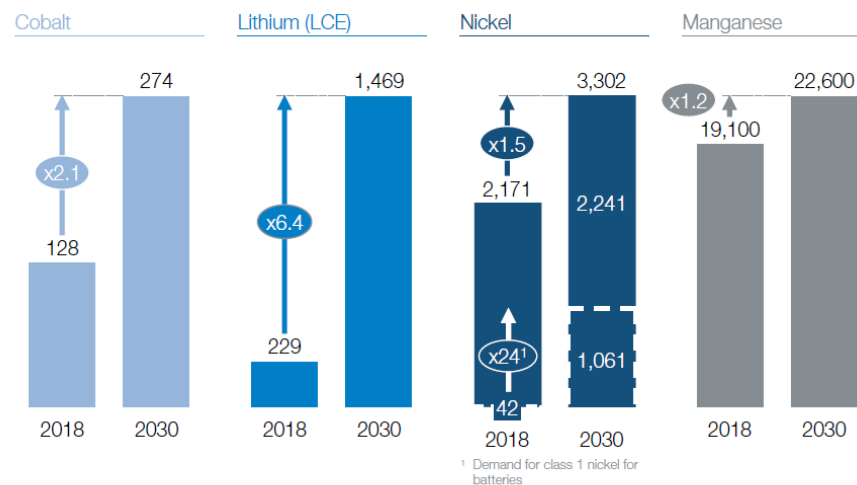


Figure 18: Raw material demand in kt·a⁻¹ in the base case. (Heid & Hertzke, 2019)

3.3 What batteries to expect for recycling?

This chapter has thus far mainly focused on present day and expected sales of various cell chemistries. If an estimate must be made of what type of batteries can be expected for recycling in a certain time span in the future, the expected total lifetime of the various batteries must also be estimated. In this paragraph this matter is looked into more closely. As it turns out, at present a lot of practical data is still missing though.

For the first life of batteries a relatively robust prediction of the total life expectancy can be made if (and only if) the practical use of the 'average' battery is known. At present this is still developing, and only partly known. Factors like how far the users will discharge the batteries before recharging and what type of recharging all have considerable influence on when to expect the batteries sold today as input material for the recycling process (lifetime).

Typical questions for the first life in a mobile application:

- is the battery on average mildly loaded (charged and discharged with modest current densities without too deep discharges) or not?
- how often per month is the battery (partially) cycled (discharge-charge)?
- will it be fast-charged every now and then? etc.

In case the battery is in a passenger car, and the user takes some care of the electric vehicle, the car battery can easily last 400,000 km before the residual battery capacity reaches 80% of the original (= technical end of life). Perhaps there will be an earlier write-off though (e.g. through introduction of better battery technology or safety concerns / recall by manufacturer for certain aging battery packs that may have shortcomings in design or construction).

If the battery is used in a heavy duty vehicle, it will be used more intensely. In such a professional application is much more cost-driven, and optimum care will be taken to get the most benefit from the (relatively expensive) batteries through e.g. conditioning of the battery pack, optimized battery and load management. Further, second life for the batteries will be competing with recycling. Estimates are that the price reduction of batteries getting swapped for new ones is likely to be 30-70% of the initial cost. The price will compete with 'new' battery technologies being sold into the stationary storage market.

Given that the EOL conditions are much more favorable for second life (40%), this will delay these batteries reaching recycling. Because of the replacement rate, and volume, not all automotive batteries will be able to go to second life (excess of supply). This will push the price down further, but ultimately reduce the overall demand between the two markets.

In other applications of Li-ion batteries, will be used stationary in a so called Energy Storage System (ESS), and batteries for it may be “new” as well as “second life” ones as well. These ESS are upcoming as part of sustainable energy systems, for example as neighborhood battery. The charging/discharging requirements for these batteries can be relatively mild, and unlike mobile application, no vibrations, accelerations or large temperature gradients come on their way. On the other hand safety requirements are even stricter because ESS systems are directly integrated in the electricity grid (costly and vital infrastructure). Also they can be situated in or near dwellings so that more people are exposed for much longer periods to possible risks of the batteries (compared to the situation in an electric vehicle). At present lithium-ion batteries with LFP chemistry as well as aqueous sodium-ion batteries are preferred for this type of use. Expected service life in an ESS can be extremely long (> 25 years).

After the first life (particularly if this was in a mobile application) the battery may get a second life application. As the battery ages, the charging capacity deteriorates, and at some point the user will decide to stop using their LIB (buying new vehicle, replacing the battery etc.). At the end of life for EV applications (80% capacity of the original battery), they can still be useful in less demanding jobs (called second use if still in vehicles, or second life if in stationary), e.g. as back-up next to solar panels, windmills, in a community buffer, or buffer for charging infrastructure. Since the requirements for steady state applications are generally much lower, it may well be that the second life will be much longer than the first life, up to 2 to 5 times as long. Since these applications for LIBs are relatively short on the market (e.g. personal EV's), real world data are mostly missing (space applications might give indications, but are hardly representative).

- For the reasons outlined above, it seems reasonable to assume time a lag of between 10 to 20 years between sales and recycling. At present there are still quite a few unknowns to precisely predict the amount and/or chemistry of batteries going to be recycled. Useful models to predict the recycling demand have been made, but outcomes depend heavily on assumptions in the input. Mentioned lag between sales and recycling makes it sensible to focus a recycling-exploration in Europe, on **NMC111** (will probably be very present in first wave of end-of-first-life batteries) and LFP (for heavy duty, incl. ships) for now. This will be perfectly useful also for further developments in these families of batteries. In the first decade of industrial LIB recycling, all varieties of NMC family cells can be expected.
- More drastic changes such as the introduction of solid state electrolyte or completely new active electrode materials, will not be substantially entering the recycling process for a long time to come. This provides ample time to modify the basic processes (tuned for NMC111 and LFP) to newcomers.
- In case the new materials blend in without disrupting the process, some small adaptations may suffice. If not, special types of batteries (e.g. ultra-fast Lithium Titanate) can be separated from the main stream of batteries. In particular for solid state batteries, the recycling process may need more substantial adaptations. How exactly solid state electrolytes such as lithium phosphorus oxynitride behave in the recycling process must be examined, after which adequate modifications in the process can be made.

4. Black mass

A lithium-ion battery consists of many components and materials ranging from functional materials such as a metal casing to working materials such as cathode active material as described in Chapter 2. For the recycling of LIBs, black mass is a common intermediate product for the production of secondary raw materials. However, as a result of novelty of the recycling process of LIBs, black mass is still considered as a black box. This chapter will elaborate on the production of black mass and the resulting composition.

4.1 Black mass production

As described in the previous sections, batteries and battery cells are composed of many components and materials and depending on the application, the materials may differ.

Battery recycling is possible by different routes. However, the most preferred option presently, hydrometallurgical processing, requires a pre-treatment process. This process is designed to liberate and purify the materials of interest, the cathode active materials, in the so-called black mass fraction for optimal recovery of the metals as secondary raw materials.

A common first step for automotive batteries is discharging of the battery pack for safe handling and subsequent dismantling: the casing and most of the electronics are removed from the battery pack, leaving only battery modules or cells for further processing. Dismantling enables high-quality recycling of aluminium and iron from the casing, copper from the wiring and electronics.

The next step in pre-treatment of LIBs is mostly comminution of battery modules or cells. The most common method is a combination of shredding, crushing, grinding and sieving, yielding a crude mixture. Depending on the further processing of the mixture, the composition will be different. In case of shredding only, all materials present in battery modules and cells will be present in the black mass evidently. However, most processes yielding black mass also contain several separation techniques, targeting a single or multiple contaminants yielding a higher quality black mass with increasing number of steps. Most common is for example magnetic separation to remove iron particles from the module casing. An Eddy current separator is utilized to separate non-ferrous metals originating from current collectors. Plastics from the separator are isolated by density separation. Finally, some processes also employ a thermal process step under reduced pressure to evaporate the organic solvent from the electrolyte. Advanced processes such as chemical treatment, chemical dissolution, and supercritical fluid extraction can also be applied. (Li et al., 2021) However, although these separation steps may be included, such contaminating materials may still be present in the resulting black mass. Figure 19 represents an overview of the active cathode material's life cycle and the current recovery strategies.

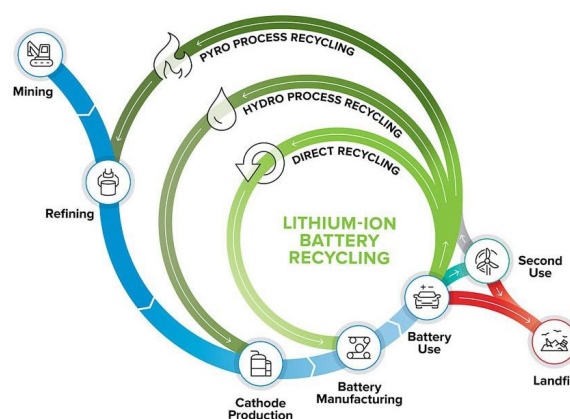


Figure 19: Life cycle of the active cathode material.

An example of black mass production is depicted in Figure 20, which illustrates the pre-treatment process by Accurec Recycling. The process contains sequential steps of discharging, pyrolysis, dry crushing, and dry sieving. (Vanderbruggen et al., 2021) It is important to note that these sequential pre-treatment steps are performed with the aim to eliminate contaminants such as plastic separators, binder particles or coarse metallic pieces from e.g. the metal casing. The more sophisticated the pre-treatment process is, the higher quality of the obtained black mass will be. A higher quality black mass contains higher weight% cathode active material and less pollutants such as separators or copper foil compared to low quality black mass.

A more detailed description of black mass production, or the pre-treatment of LIB recycling will be given in Deliverable 6.2.1 of the project.

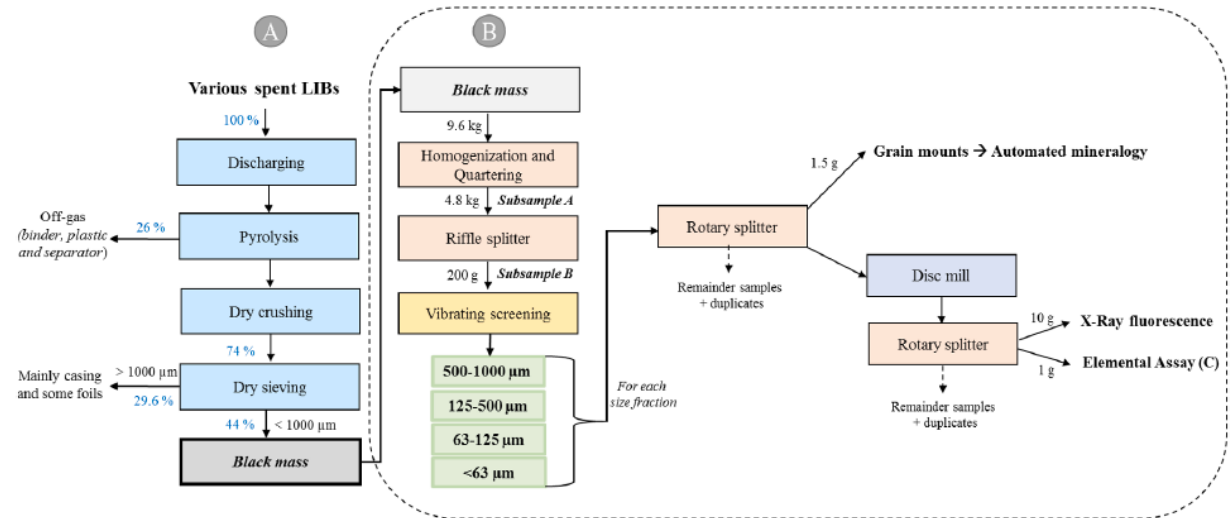


Figure 20: Flowsheet for back mass production at Accurec Recycling GmbH (part A) and subsequent size size fractioning for analysis (part B). Figure copied from reference (Vanderbruggen et al., 2021)

4.2 Composition of black mass

Black mass does not have a defined composition, however, it consists of, but is not limited to, cathode active material of pre-treated LIBs. The term black mass is explained by the presence of graphite from the anode material: as graphite has similar physical properties as the cathode active materials, it remains in the material stream and gives the material a black appearance. However, depending on the composition of the LIBs processed, cathode materials also contribute to the color as LCO is also black. Black mass is a fine powder as the materials are shredded, crushed and/or ground finely during the pre-treatment process. Figure 21 shows a photo of a black mass sample originating from a mixture of batteries from household apparatus as well as automotive LIBs. The photo clearly shows that the black mass sample contains a variety of materials, indicated by a few lighter colored particles. (Wu et al., 2020)



Figure 21: A photo of a black mass sample. The photo is copied from reference (Wu et al., 2020).

Another study shows that the particle size of black mass may differ: the study analyzed the particle size distribution of three samples, one of which showing that 95 % of the particles was smaller than 30 μm , and the most coarse sample contained particles up to 250 μm . (Dadé et al., 2022) This is of course a result from the pre-treatment process: more grinding and finer sieving results in smaller particles.

The higher the quality of the black mass, the more it resembles (a mixture of) cathode materials. In addition to pre-treatment steps, the sorting process prior to pre-treatment also has a significant impact on the composition of the black mass as sorting prevents different battery chemistries from being mixed. Table 3 shows the elemental composition of black mass batches produced by Stena Recycling International AB in Sweden. (Babanejad et al., 2022) These batches are produced from very defined LIB waste streams, containing either LiCoO_2 (LCO) or LiNiMnCoO_2 (NMC 111) batteries. Consequently, the black mass produced from waste LCO contains a high weight% of cobalt and obviously no nickel or manganese are present. The black mass produced from NMC batteries contain all three mentioned metals.

Table 3: Chemical composition of black mass obtained from processed LCO batteries and NMC batteries. Table is copied from reference (Babanejad et al., 2022)

Sample (wt%)	Li	Co	Ni	Mn	Al	Cu	Si	P	F	C
LCO < 150 μm	3.8	31.4	0.0	0.0	0.4	0.4	1.6	0.4	2.1	43.8
LCO 150–700 μm	4.0	32.3	0.0	0.0	0.9	0.6	1.6	0.5	2.6	35.4
NMC < 150 μm	6.3	17.3	15.5	15.1	0.0	0.8	1.3	0.4	4.9	12.8
NMC 150–700 μm	3.6	8.0	7.3	7.6	0.2	1.6	1.0	0.6	6.5	43.2

Table 3 also highlights that although the pre-treatment process at Stena Recycling International includes mechanical separation and subsequent heat treatment at 250–300 $^{\circ}\text{C}$ (to remove the electrolyte), pollution from other LIB components is still present in the samples:

- The high amount of carbon (C) can be attributed to the graphite from the anode
- Traces of aluminum (Al) and copper (Cu) most likely originate from the current collectors
- Silicon (Si) might arise from additive material in the anode

- Fluorine (F) is a main component of PVDF binder but might also arise from the presence of LiPF_6 electrolyte, similar to phosphorus (P)

It is important to note that when there is poor sorting, different battery chemistries will be present in the LIB waste material, resulting in a broader mixture of different metals in the black mass. When a higher number of elements are present in high concentration, targeted metals are more easily contaminated with non-target metals. The process then becomes more complex, more process steps and more chemicals needed, such that it becomes more expensive. Therefore, sorting is mandatory for an economically viable process. Figure 22 shows an example of the analysis of a black mass sample originating from a poorly sorted batch of spent LIBs. The sample is screened using a scanning electron microscope coupled with a Quantitative Evaluation of Minerals System to analyze the composition of each separate particle, focusing on inorganic matter only. It clearly shows that the materials in the battery cells have been finely comminuted or more finely sieved: 95 % of the particles is smaller than 150 μm . The table on the right shows the variety of materials discovered in the sample: not only cathode active materials of various chemistries are found, but very fine particles of copper and aluminum oxide are detected as well. The sample most probably also contains non-LIB materials as well, as quartz and silicates cannot be ascribed to LIBs. (Dadé et al., 2022)

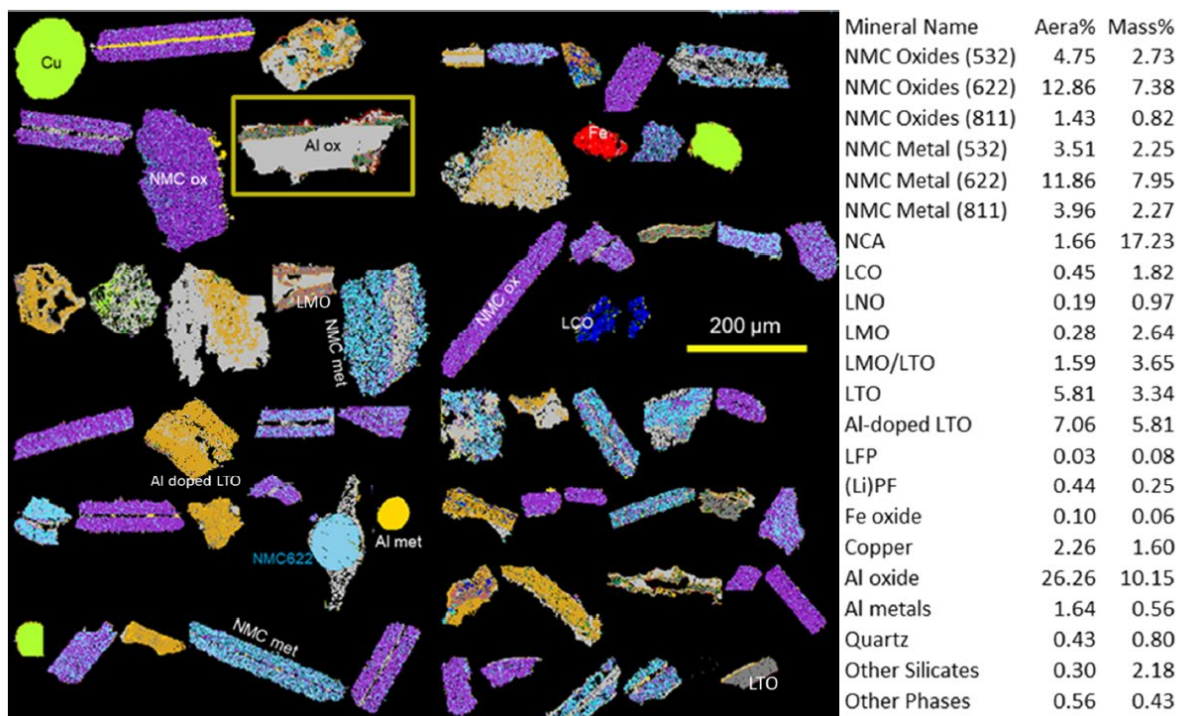


Figure 22: Selection of particles present in black mass visualized using a SEM coupled with a Quantitative Evaluation of Minerals by Scanning electron microscopy system (QEMSCAN®) with the corresponding material analysis of the sample. The figure is copied from reference (Dadé et al., 2022)

The composition described above is relevant to the LIBs that are currently being processed to black mass. Most batches of black mass will contain elements such as cobalt, nickel, lithium and manganese. However, as new generations of LIBs will be put on market, the composition of black mass will be affected. Currently, most batteries contain a large amount of cobalt as most batteries contain a LCO or NMC111 cathode chemistry. However, most LIBs put on market nowadays, contain less cobalt, such

as the NMC622 or NMC811 cathode chemistry, consequently lowering the cobalt contents while increasing the nickel contents.

As LIB technologies further develop, the black mass composition will become more complicated. Materials such as mixed anode materials of silicon and graphite become more abundant, but also the presence of solid electrolyte may complicate the processing of the LIB. In the latter case, the materials may end up in the black mass fraction. However, the material composition of solid electrolytes may be quite different from the metal containing active materials: the latter are still easily dissolved in the dissolution process step, whereas the electrolyte material remains unaffected, yielding larger solid material flows to be removed from the recycling process.

In conclusion, it is not possible to exactly define the composition of black mass, since the composition is dependent on many factors. These factors include the degree of sorting of the spent LIBs, and the quality and number of pre-treatment steps. If the LIB waste stream contains exclusively only one LIB type (e.g. LiCoO_2), it is most likely that the black mass will only contain cathode components from this battery type (in this case lithium and cobalt). Depending on the type and number of pre-treatment steps, materials from other components of the LIB battery such as the binder, current collector of anode are also present in the black mass.

4.3 Analysis of black mass samples

The project proposal also describes a practical analysis of black mass samples. However, due to limited suppliers of black mass and the maturity of the recycling market of LIBs in the Netherlands, we did not yet succeed in obtaining a representative sample of black mass. As the project is not finished, the project team aims to obtain a representative sample still in order to get a complete picture of black mass.



5. Conclusion

In the past decades, different types of cathode active materials have been developed, mostly focused on the use of lithium, cobalt, nickel and manganese, yielding complex products containing a wide variety of materials. However, a number of components, casing and electronics, are manually dismantled for high-quality recycling. Other components, such as the cell casing, current collectors and active materials cannot be dismantled, but are comminuted and in this way mixed together. Most recycling technologies employ a pre-treatment step, including several separation steps, preceding a hydrometallurgical processing route, which yields an intermediate product, black mass. Black mass mostly contains the active materials from the cathode and anode, comprising approximately 25 % of the total battery weight, but also small particles from current collectors and separators for example. The latter represent circa 40 % of the total battery weight, but are mostly separated from the black mass fraction in the pre-treatment process.

Studies for market developments show divergent prospects, some similarities are observed. For electric vehicles in particular, but also for many other high-performance applications, LIBs with NMC cathode active materials remains a relevant and interesting variety to design and develop recycling process technology. The experience and technology developed can easily be applied to other varieties of this popular battery type within Li-ion batteries. For heavy duty applications, the LFP battery chemistry will become predominant.

From an economic viewpoint, focussing recycling efforts on the batteries with costly cathode materials, thus high cobalt and nickel content, makes the most sense. Because of product liability, quite some manufacturers may do the recollection and recycling of end-of-life LIBs in house. For LFP LIBs, the economic attractiveness is at present much lower. The need at medium-long term for recycling technology, is high though, because the supply of end of life LFP batteries is coming up right now. Future battery technologies will complicate the design of a one-process-fits-all design: new battery technologies use additional elements, titanium in the case of LTO anodes and silicon for Si-C anodes, or contain more complicated structures, in the case of solid state batteries. However, on the short term, these battery technologies are not expected to be recycled as they are not yet produced on an industrial scale. When such batteries are produced at such scale or reach end-of-life, sorting preceding shredding becomes important.

The composition of the intermediate product of battery recycling technologies, black mass, is as mentioned strongly dependent on the chemistry of batteries comminuted in the pre-treatment process. A mix of battery chemistries fed to the pre-treatment process yields a wide variety of elements in the black mass, complicating the metal recovery process as more 'contaminants' are introduced and forces recyclers to implement a thorough sorting step in the process. In addition, the pre-treatment separation steps are also crucial for the efficiency of the recovery of cathode specific materials.



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